

(19) World Intellectual Property Organization  
International Bureau



(43) International Publication Date  
27 November 2003 (27.11.2003)

PCT

(10) International Publication Number  
**WO 03/097723 A1**

- (51) International Patent Classification<sup>7</sup>: C08J 5/18, C08G 69/40, C11D 17/04
- (21) International Application Number: PCT/US03/15106
- (22) International Filing Date: 14 May 2003 (14.05.2003)
- (25) Filing Language: English
- (26) Publication Language: English
- (30) Priority Data:  
60/380,380 14 May 2002 (14.05.2002) US
- (71) Applicant: E.I. DU PONT DE NEMOURS AND COMPANY [US/US]; 1007 Market Street, Wilmington, DE 19898 (US).
- (81) Designated States (*national*): AE, AG, AL, AM, AT, AU, AZ, BA, BB, BG, BR, BY, BZ, CA, CH, CN, CO, CR, CU, CZ, DE, DK, DM, DZ, EC, EE, ES, FI, GB, GD, GE, GH, GM, HR, HU, ID, IL, IN, IS, JP, KE, KG, KP, KR, KZ, LC, LK, LR, LS, LT, LU, LV, MA, MD, MG, MK, MN, MW, MX, MZ, NI, NO, NZ, OM, PH, PL, PT, RO, RU, SC, SD, SE, SG, SK, SL, TJ, TM, TN, TR, TT, TZ, UA, UG, UZ, VC, VN, YU, ZA, ZM, ZW.
- (84) Designated States (*regional*): ARIPO patent (GH, GM, KE, LS, MW, MZ, SD, SL, SZ, TZ, UG, ZM, ZW), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, BG, CH, CY, CZ, DE, DK, EE, ES, FI, FR, GB, GR, HU, IE, IT, LU, MC, NL, PT, RO, SE, SI, SK, TR), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, GQ, GW, ML, MR, NE, SN, TD, TG).
- (72) Inventor: PAGILAGAN, Rolando, Umali; 20 Mustang Acres, Parkersburg, WV 26104 (US).
- (74) Agent: HAMBY, William, H.; E.I. Dupont De Nemours And Company, Legal Patent Records Center, 4417 Lancaster Pike, Wilmington, DE 19805 (US).
- Published:  
— with international search report
- For two-letter codes and other abbreviations, refer to the "Guidance Notes on Codes and Abbreviations" appearing at the beginning of each regular issue of the PCT Gazette.*

(54) Title: PACKAGING AND CONTAINERS MADE OF WATER-SOLUBLE POLYAMIDES AND PROCESSES FOR THEIR MANUFACTURE

(57) Abstract: Packaging materials made from water-soluble nylons are disclosed, that readily contain materials such as caustic chemicals and upon exposure to water dissolve to provide for the release of the chemical into an aqueous environment. The materials are made from select polyether diamines and select aliphatic dicarboxylic acids.

WO 03/097723 A1

**PACKAGING AND CONTAINERS MADE OF WATER-SOLUBLE  
POLYAMIDES AND PROCESSES FOR THEIR MANUFACTURE**

**FIELD OF THE INVENTION**

5  
This invention relates to packaging made from water-soluble nylon compositions and suitable for containing materials of interest. More particularly, this invention relates to such packaging that adequately contains the material until  
10 deposited into water, after which the material is released into an aqueous environment, and processes for the manufacture thereof.

**BACKGROUND OF THE INVENTION**

15 Stringent environmental regulations on chemical emissions and concern for worker exposure to chemicals have intensified the effort to eliminate emissions and minimize physical contact with sensitive materials. There is also a similar desire to limit exposure of consumers to aggressive and corrosive chemicals from a public health perspective. One approach to minimize this exposure during handling of  
20 chemicals is the use of pre-packaged unit doses using water-soluble packaging materials. Applications for unit dose packaging are convenient and limit the exposure of the user to different types of chemicals (such as laundry, dishwater or other detergents, pesticides, agriculture chemicals, bleaches, and the like). Presently, partially hydrolyzed polyvinylalcohol (PVA) is used for a number of these  
25 applications. However, PVA has limited chemical resistance and thermal stability and is not amenable to film formation by melt extrusion processes such as film casting from melt or blown film extrusion. A combination of moisture and elevated temperatures or the presence of acids and bases can catalyze the hydrolysis of the acetate groups which results in reduced solubility in cold water. For the same reason  
30 PVA also has poor shelf life and its solubility in water is adversely affected by storage time and conditions. There is a need for a polymeric composition that is consistently water-soluble to suit these applications.

Water-soluble polymers are either natural (biopolymers) or man-made. To be water-soluble these polymers are highly polar in nature. A large number of functional groups are used to impart polarity and, in turn, water-solubility to various polymers.

5 Functional groups such as amines, hydroxyl, sulfonic acids, and carboxylic acids and their salts are commonly used to solubilize polymers. However, it is not uncommon for the reactive functional groups such as acids and amines to react with other acids and bases that they come in contact with during end-use, and this leads to changes in properties such as solubility. For an extensive review of this subject see "Water-

10 Soluble Polymers", Encyclopedia of Polymer Science & Engineering, Volume 17, pages 730-784, Second Edition, John Wiley & Sons (1989).

There is a long-felt need in the field for the development of a polyamide-based composition for such applications. Nylons are well known for their strength,

15 toughness, abrasion resistance, lubricity, and chemical resistance. The use of nylons in basic packaging applications is widespread because of the aforementioned properties. See generally, Kohan, M. I., "Nylon Plastics Handbook", Hanser/Gardner Publications, Inc., 1995, pages 514, 540, & 568-569. However their adaptation towards applications requiring solubility in water to date has not been particularly

20 effective.

The patent literature includes various teachings regarding water-soluble nylons. U.S. 4,895,660 describes water-soluble sulfonated aromatic polyamides and polyureas that are cross-linked ionically with multi-valent metals for membranes,

25 coatings, and adhesives. Japanese Patent Application 56-93704 describes a photosensitive composition comprising a water-soluble polyamide containing sodium sulfonate groups, a polymerizable unsaturated compound, and a sensitizer for printing plate applications. Japanese Patent Application 98007903A claims the use of alcohol-water solutions of nylons commonly known as PA66, PA46, PA6, and PA12 with a

30 water-soluble methoxymethylated nylon, and thiocyanate salts in alcohol-water solvent as wiper blade coatings to improve performance and durability of the blades.

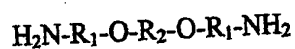
U.S. 4,323,639 and U.S. 5,688,632 are both directed to water-soluble copolyamides containing polyether segments of 150 to 1500 molecular weight. These polyether-amide segments are obtained from polyether diamines and aliphatic dicarboxylic acids. These water-soluble polyamides are used in conjunction with  
5 photopolymerizable compound and a photoinitiator for printing plate applications.

It is well known in organic chemistry that ethers are relatively chemically unreactive compared to functionalities such as acids, amines, and hydroxyls. A water-soluble polyamide containing polyoxyethylene segments for water solubility  
10 would possess chemical inertness and thermal stability. These two characteristics would be advantageous in shaped-article production such as extrusion, blow-molding, and injection molding operations. However, up to now there has been no report in the literature on the use of water-soluble nylons containing polyoxyethylene segments for packaging and container applications and as a polymeric binder for tablets and  
15 briquettes.

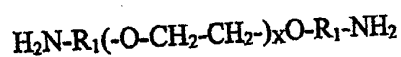
It is an object of the present invention to provide a water-soluble nylon that can be incorporated into unit-dose packaging applications containing any of a variety of materials. It is a further object of the present invention to provide such materials  
20 that retain their integrity under ambient conditions and when immersed in water predictably solubilize and thereby release the contained material into aqueous solution. A feature of the present invention is its utility both as a packaging material (as envelopes, pouches and the like) and as a binder (for tablets, briquettes and the like). It is an advantage of the present invention that chemicals suitably packaged  
25 with materials described herein are not placed in contact with or only minimally contact persons handling the packaging. A further advantage of the present invention is its suitability for any of a number of conventional molding applications, including blow molding. These and other objects, features and advantages of the present invention will become better understood upon having reference to the description of  
30 the invention herein.

### SUMMARY OF THE INVENTION

There is disclosed and claimed herein a packaging material comprising a water-soluble polyamide with a solubility in water at 23 C of at least 1.0 weight percent and derived from the reaction of adipic acid and ether diamines with a molecular weight of 148 to 396 and represented by the general formulas



wherein  $\text{R}_1$  and  $\text{R}_2$  are either  $-\text{CH}_2-\text{CH}_2-$  or  $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$  ;



wherein  $\text{R}_1$  is either  $-\text{CH}_2-\text{CH}_2-$  or  $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$

and X has an average value of 2 to 6; and mixtures thereof.

Those of skill in the art will appreciate that  $\text{R}_1$ 's in the above formula are usually the same but can be different.

Moreover, the packaging materials disclosed and claimed herein and described in the processes also disclosed and claimed herein preferably have water soluble polyamides with a relative viscosity of less than 50 (and most preferably between 10 and 35). The solubility in water of such polyamides is at a rate such that a 5-10 mil film formed of this material will dissolve preferably in less than an hour (and preferably in less than 30 minutes).

## DETAILED DESCRIPTION OF THE INVENTION

Copolyamides of the above polyamide with other polyamide-forming  
5 comonomers can also be used herein. These other nylon forming comonomers may  
be incorporated provided these comonomers do not adversely affect the water  
solubility of the resulting polyamide. These added comonomers may include other  
polyamide forming comonomers such as lactams, polyether diamines, polyether  
10 diacids, alkylene diamines, and alkylene dicarboxylic acids. The solubility in water  
of these nylons is influenced not only by the amount of the polyetherdiamines and the  
nature of the dicarboxylic acids but the molecular weight as well. Additives such as  
heat and UV stabilizers, anti-oxidants, plasticizers, lubricants, and catalyst may be  
used if desired to enhance the properties of the polymer or aid the polymerization  
15 process. Those having skill in the art to which this invention pertains will readily  
appreciate how much and in what manner these additives may be incorporated.

The water-soluble packaging articles disclosed herein may be fashioned in any  
of a variety of forms including without limitation films, bags, pouches, bottles, and  
jars, and as a binder for water-soluble tablets and briquettes and similar applications.  
20 In the latter application, the binder on exposure to water disintegrates, thereby  
providing for a release of the previously bound material into water.

There is also disclosed and claimed herein processes for the manufacture of  
these various packaging materials. The polyamide described above is formed as a  
25 film. The film is then shaped into a container suitable for placement of the chemical  
or other material of interest to be contained. Once the material is deposited into the  
container, the container is sealed to retain the material within it. Those having skill in  
this field will readily appreciate the various techniques for film formation, and  
container shaping and sealing.

30

Another process disclosed and claimed herein pertains to the manufacture and use of these polyamides as binders for tablets, briquettes and the like. The material to be packaged is presented, after which the polyamide is interspersed therewithin. The resulting product is shaped into a solid formation of interest. Formative techniques for the tablets and briquettes are again well understood by those having skill in this field, and generally include the initial development of a paste or slurry and subsequently removing the water and/or applying pressure to provide a solidified material. Prior to solidification the material can be shaped in designs and configurations of interest.

10 **EXAMPLES**

**Preparation of the Nylon Resins**

The nylon polymerization was carried out using standard nylon polymerization process that is well-known in the art (See Kohan, M.L., "Nylon  
15 Plastics Handbook" Hansen/Gardner Publications, Inc. [1995] pages 17-20 & 34-45). As is well known in the art, the stoichiometry of the ingredients was determined and controlled using pH measurements. The molecular weight during polymerization, as indicated by relative viscosity (RV), was controlled by controlling pH, use of  
20 atmospheric, nitrogen, or vacuum finishing after pressure reduction. Usually, the molten polymer is quenched in water and then cut into pellets. However, because these nylons are water-soluble the molten polymer is either allowed to cool under ambient conditions or dropped onto a bed of ground dry ice for cooling.

### Testing

5     The relative viscosity in formic acid (RV) of an 8.4% solution was determined at 25 C using a Brookfield Viscometer.

10    The solubility in room temperature water (23 C) at 10% concentration was determined by mixing 10 weight percent of the polymer with 90 weight percent demineralized water and stirring at room temperature. The solution was allowed to sit at room temperature and the solution was observed for any sign of precipitation.

### Comparative Example A

15    In a beaker provided with a stirrer, 300 ml. of demineralized water and 222.0 g of triethyleneglycol diamine ( $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{NH}_2$ ) were mixed and heated to 60 – 70 C with stirring. To the mixture was added slowly 345.0 g dodecanedioic acid. An additional 200 ml of de-mineralized water was added. When all the dodecanedioic acid was dissolved the pH was adjusted to 7.15 by addition of 4.1 g of triethyleneglycol diamine (TEGD). The solution was then  
20    introduced into a 3,785 ml autoclave where the solution was heated slowly until the pressure in the autoclave reached 250 psig. At this point, steam was slowly vented while heating was continued. When the batch temperature reached 225 C, the steam venting was increased so as to lower the pressure to atmospheric pressure in 45 minutes but at a rate such that the batch temperature would continue to increase as it  
25    was being concentrated. The polymer was then subjected to 21.0 "of vacuum for 60 minutes. At the end of 60 minutes the batch temperature was 270 C. The autoclave was then pressured with nitrogen and forced out of the autoclave and into a pan. The polymer was allowed to cool to room temperature. The polymer had an RV of 15.7.

30    Using the same procedure (but with minor variations in temperature, vacuum and hold time as appropriate by those of skill in the art, to obtain the desired



molecular weight) as Comparative Example A, Comparative Examples B and C were prepared using the appropriate ingredients. Results are shown below.

SAMPLE	COMPOSITION	CATALYST	RV	SOLUBILITY
Comparative Example C	TEGD, 9	None	14.9	Insoluble
Comparative Example B	TEGD, 10	None	13.3	Insoluble
Comparative Example A	TEGD, 12	None	15.7	Insoluble

5 Example 1

In a beaker provided with a stirrer, 300 ml. of de-mineralized water and 444.0 g of TEGD were mixed and heated to 60 – 70 C with stirring. To the mixture was added slowly 438.0 g of adipic acid. An additional 100 ml of de-mineralized water  
10 was added. When all the adipic acid was dissolved the pH was adjusted to 7.25 by addition of 7.2 g of TEGD. The solution was then introduced into a 3,785 ml autoclave where the solution was heated slowly until the pressure in the autoclave reached 250 psig. At this point, steam was slowly vented while heating was continued. When the batch temperature reached 225 C, the steam venting was  
15 increased so as to lower the pressure to atmospheric pressure in 45 minutes but at rate such that the batch temperature would continue to increase as it was being concentrated. The polymer was then subjected to 19.5 " of vacuum for 60 minutes. At the end of 60 minutes the batch temperature was 270 C. The autoclave was then pressured with nitrogen and forced out of the autoclave and into a pan. The polymer  
20 was allowed to cool to room temperature. The polymer had an RV of 12.9.

Example 2

5        In a beaker provided with a stirrer, 1997.0 g of de-mineralized water and 740.0 g of TEGD were mixed with stirring. To the mixture was added slowly 730.0 g of adipic acid. When all the adipic acid was dissolved 0.37 g of sodium hypophosphite monohydrate (SHP monohydrate) was added. The pH of the salt solution was 7.10. An 830.0 g portion of the salt was then introduced into a 3,785 ml autoclave where  
10       the solution was heated slowly until the pressure in the autoclave reached 250 psig. At this point, steam was slowly vented while heating was continued. When the batch temperature reached 225 C, the steam venting was increased so as to lower the pressure to atmospheric pressure in 45 minutes but at a rate such that the batch temperature would continue to increase as it was being concentrated. The polymer  
15       was then held at atmospheric conditions for 20 minutes. At the end of 20 minutes the batch temperature was 255 C. The autoclave was then pressured with nitrogen and forced out of the autoclave and into a pan with ground dry ice. The polymer had an RV of 14.0.

20       Example 3 and Example 4 were prepared under the same procedure as Example 2 with the exception that vacuum was used for the finishing step. The results are shown below.

SAMPLE	COMPOSITION	CATALYST (1)	RV	SOLUBILITY
Example 1	TEGD,6	None	12.9	Soluble
Example 2	TEGD,6	210 ppm	14.0	Soluble
Example 3	TEGD,6	349 ppm	20.5	Soluble
Example 4	TEGD,6	210 ppm	22.8	Soluble

(1) Sodium hypophosphite monohydrate

5        Examples 1 to 4 and Comparative Examples A, B, and C demonstrate that the incorporation of ether amine segments in the polymer alone is not sufficient to achieve water solubility. The proper selection of the dicarboxylic acid structure is necessary to obtain water soluble nylons.

10    Example 5

15        In a beaker provided with a stirrer, 300 ml of de-mineralized water and 278.2 g of TEGD were mixed and heated to 60 – 70 C with stirring. To the mixture was added slowly 274.5 g of adipic acid. When the adipic acid has dissolved, 269.0 g of caprolactam solution with an 81.86 weight percent concentration was added. The pH was then adjusted to 7.35 by addition of 4.1 g of TEGD. The solution was then introduced into a 3,785 ml autoclave where the solution was heated slowly until the pressure in the autoclave reached 250 psig. At this point, steam was slowly vented while heating was continued. When the batch temperature reached 225 C, the steam venting was increased so as to lower the pressure to atmospheric pressure in 45 minutes but at a rate such that the batch temperature would continue to increase as it was being concentrated. The polymer was then subjected to 22.0" to 22.5" of vacuum for 60 minutes. At the end of 60 minutes the batch temperature was 268 C. The autoclave was then pressured with nitrogen and forced out of the autoclave and into a

pan. The polymer was allowed to cool to room temperature. The polymer had an RV of 17.7. The results are shown below.

SAMPLE	COMPOSITION	MOLE RATIO	CATALYST (1)	RV	SOLUBILITY
Example 5	TEGD,6/6	50/50	None	17.7	Soluble
Example 6	TEGD,6/6	50/50	349 ppm	25.6	Soluble (2)
Example 7	TEGD,6/6	70/30	None	15.3	Soluble
Example 8	TEGD,6/6	80/20	None	14.1	Soluble
Comparative Example D	TEGD,6/6	40/60	None	19.0	Insoluble

- 5 (1) Sodium hypophosphite monohydrate  
(2) Soluble but went to solution much slower than Example 5

Examples 5, 6, 7, 8, and Comparative Example D illustrate that the ratio of comonomers affect the solubility of the copolymers in water. Example 5 and  
10 Example 6 also demonstrate that the RV (molecular weight) of the polymer also affects the rate of solution. The higher molecular weight results in slower dissolution rate.

Examples 9 to 11 and Comparative Examples E, F, G and H

15

Using the same procedure as in previous examples, and controlling RV as previously discussed herein various copolymers with nylon 66, 46, and 2-methylpetamethylenediamine,6 were prepared. The results are shown below.

SAMPLE	COMPOSITION (1)	MOLE RATIO	CATALYST (2)	RV	SOLUBILITY
Example 9	TEGD,6/6,6	90/10	None	14.1	Soluble
Comparative Example E	TEGD,6/6,6	80/20	None	15.5	Insoluble
Comparative Example F	TEGD,6/6,6	70/30	152 ppm	16.5	Insoluble
Example 10	TEGD,6/2MPMD,6	70/30	None	15.1	Soluble
Comparative Example G	TEGD,6/2MPMD,6	65/35	None	17.7	Insoluble
Example 11	TEGD,6/4,6	70/30	None	9.4	Soluble
Comparative Example H	TEGD,6/4,6	50/50	None	10.5	Insoluble

(1) 2MPMD stands for 2-methylpentamethylenediamine

5 (2) Sodium hypophosphite monohydrate

Examples 9, 10, 11, and Comparative Examples E, F, G, and H illustrate again that the solubility in water of copolymers is dependent on the type and amount of comonomer used.

10

#### Example 12

In a beaker provided with a stirrer, 500 ml of demineralized water and 264.0 g of 1,2-bis(gamma-aminopropoxy) ethane ( $\text{H}_2\text{N}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-\text{CH}_2-\text{O}-\text{CH}_2-$

CH<sub>2</sub>-CH<sub>2</sub>-NH<sub>2</sub> ) were mixed and heated to 60 - 70 C with stirring. To the mixture was added slowly 219.0 g of adipic acid. When the adipic acid has dissolved the pH was adjusted to 7.12 by adding 26.0 g of 1,2-bis(gamma-aminopropoxy) ethane (BGAE) and 5.0 g of adipic acid. . Those having skill in the art will readily appreciate that different grades of BGAE (and as described later, POE-DPA 220) are available, and these have differing levels of monoamines and triamines associated with them. However these byproducts have minor effects in adjusting the pH level so that the pH of interest is readily attained. This may have an effect on the polymerization process, and some adjustments to this process may be necessary to achieve the desirable molecular weight, again as is well appreciated by the person of skill. The solution was then introduced into a 3,785 ml autoclave where the solution was heated slowly until the pressure in the autoclave reached 250 psig. At this point, steam was slowly vented while heating was continued. When the batch temperature reached 225 C, the steam venting was increased so as to lower the pressure to atmospheric pressure in 45 minutes but at a rate such that the batch temperature would continue to increase as it was being concentrated. The polymer was then subjected to 21 -22" of vacuum for 60 minutes. At the end of 60 minutes the batch temperature was 258 C. The autoclave was then pressured with nitrogen and forced out of the autoclave and into a pan. The polymer was allowed to cool to room temperature. The polymer had an RV of 7.7.

### Example 13

In a beaker provided with a stirrer, 500 ml of de-mineralized water, 246.4 g of BGAE, and 82.0 g of caprolactam solution with an 82.68 weight percent concentration were mixed and heated to 60 - 70 C with stirring. To the mixture was added slowly 204.4 g of adipic acid. When the adipic acid has dissolved the pH was adjusted to 7.09 by adding 19.5 g of BGAE. The solution was then introduced into a 3,785 ml autoclave where the solution was heated slowly until the pressure in the autoclave reached 250 psig. At this point, steam was slowly vented while heating was continued. When the batch temperature reached 225 C, the steam venting was

increased so as to lower the pressure to atmospheric pressure in 45 minutes but at a rate such that the batch temperature would continue to increase as it was being concentrated. The polymer was then subjected to 21" of vacuum for 60 minutes. At the end of 60 minutes the batch temperature was 264 C. The autoclave was then  
5 pressured with nitrogen and forced out of the autoclave and into a pan. The polymer was allowed to cool to room temperature. The polymer had an RV of 8.7.

#### Comparative Example I

10 In a beaker provided with a stirrer, 500 ml of de-mineralized water, 211.2 g of BGAE, and 164.0 g of caprolactam solution with an 82.68 weight percent concentration were mixed and heated to 60 - 70 C with stirring. To the mixture was added slowly 175.2 g of adipic acid. When the adipic acid has dissolved the pH was adjusted to 7.15 by adding 12.0 g of BGAE. The solution was then introduced into a  
15 3,785 ml autoclave where the solution was heated slowly until the pressure in the autoclave reached 250 psig. At this point, steam was slowly vented while heating was continued. When the batch temperature reached 225 C, the steam venting was increased so as to lower the pressure to atmospheric pressure in 45 minutes but at a rate such that the batch temperature would continue to increase as it was being  
20 concentrated. The polymer was then subjected to 18-19" of vacuum for 60 minutes. At the end of 60 minutes the batch temperature was 264 C. The autoclave was then pressured with nitrogen and forced out of the autoclave and into a pan. The polymer was allowed to cool to room temperature. The polymer had an RV of 10.7. The results are shown below.

SAMPLE	COMPOSITION (1)	MOLE RATIO	RV	SOLUBILITY
Example 12	BGAE,6		7.7	Soluble
Example 13	BGAE,6/6	70/30	8.7	Soluble
Comparative Example I	BGAE,6/6	50/50	10.7	Insoluble

(1) BGAE is an acronym for 1,2-bis(gamma-aminopropoxy) ethane

5

Examples 12, 13, and Comparative Example I show that replacement of TEGD with BGAE also affords a water-soluble polyamide. Furthermore, copolymers of BGAE,6 behaves similarly with the copolymers of TEGD,6.

#### 10 Example 14

In a beaker provided with a stirrer, 300 ml of de-mineralized water and 176.0 g of POE-DPA220 were mixed and heated to 60 - 70 C with stirring. This diprimary amine has the following structure (H<sub>2</sub>N-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-[polyoxyethylene]-CH<sub>2</sub>-CH<sub>2</sub>-CH<sub>2</sub>-NH<sub>2</sub>) where the polyoxyethylene unit is (O-CH<sub>2</sub>-CH<sub>2</sub>-O-CH<sub>2</sub>-CH<sub>2</sub>-O) and has a molecular weight of 220. To the mixture was added slowly 116.8 g of adipic acid. The pH of the solution was 6.9. To the solution was then added 0.074 g of sodium hypophosphite monohydrate. The salt solution was then introduced into a 3,785 ml autoclave where the solution was heated slowly until the pressure in the autoclave reached 250 psig. At this point, steam was slowly vented while heating was continued. When the batch temperature reached 225 C, the steam venting was increased so as to lower the pressure to atmospheric pressure in 45 minutes but at a rate such that the batch temperature would continue to increase as it was being

20



concentrated. The polymer was then held at atmospheric pressure for 20 minutes. At the end of 20 minutes the batch temperature was 249 C. The autoclave was then pressured with nitrogen and forced out of the autoclave and into a pan of dry ice. The polymer had an RV of 7.8 and was soluble in water at room temperature.

5

#### Comparative Example J

In a beaker provided with a stirrer, 200 ml of de-mineralized water and 88.0 g of POE-DPA220 were mixed and heated to 60 - 70 C with stirring. To the mixture was added slowly 58.4 g of adipic acid. The pH of the solution was adjusted to 6.72 by addition of 5.0 g of POE-DPA220. To the solution were added 117.6 g of a caprolactam solution with a concentration of 74.69 weight percent, 186.8 g of nylon 6,6 salt with a concentration of 31.35 weight percent, and 0.88 g of sodium hypophosphite monohydrate. The salt solution was then introduced into a 3,785 ml autoclave where the solution was heated slowly until the pressure in the autoclave reached 250 psig. At this point, steam was slowly vented while heating was continued. When the batch temperature reached 225 C, the steam venting was increased so as to lower the pressure to atmospheric pressure in 45 minutes but at a rate such that the batch temperature would continue to increase as it was being concentrated. The polymer was then held at atmospheric pressure for 18 minutes. At the end of 18 minutes the batch temperature was 260 C. The autoclave was then pressured with nitrogen and forced out of the autoclave into a pan of dry ice. The polymer had an RV of 12.5.

Using the same procedure as Comparative Example J and controlling RV as previously described herein, Comparative Examples K and L were prepared using POE-DPA514 (molecular weight of 514) and POE-DPA1114 (molecular weight of 1114). The results are shown below.

SAMPLE	COMPOSITION (1)	SALT WT. RATIO	CATALYST	RV	SOLUBILITY
Comparative Example J	POE-DPA220,6/6,6/6	50/20/30	0.30 wt. %	12.5	Insoluble
Comparative Example K	POE-DPA514,6/6,6/6	50/20/30	0.30 wt. %	15.9	Insoluble
Comparative Example L	POE-DPA1114,6/6,6/6	50/20/30	0.29 wt. %	16.4	Insoluble

Comparative Examples J, K, and L are polymers containing polyether amines and are described in U.S. 4,323,639 and U.S. 5,688,632 as water-soluble. These comparative examples show that the water-soluble nylon described in the U. S. 4,323,639 and U. S. 5,688,632 are not water soluble and are not useful for the purposes of this invention.

#### 10 Examples 15 to 30

The solubility of films in 23 C and 50 C water were determined on compression molded films of TEGD,6 homopolymers and TEGD,6/6 copolymers. A 2"x 2" sample of the film was attached to a 2" x 2" window cut into an aluminum sheet. This was then immersed in 1000 ml of well-stirred water maintained at 23 C and 50 C. The time it takes for the film sample to start disintegrating and the time it takes to completely dissolve are observed and recorded. Results are shown below:

SAMPLE	COMPOSITION	MOL RATIO	RV	FILM THICKNESS (mils)	WATER TEMP (C)	TIME TO DISINTEGRATE (sec)	TIME TO DISSOLVE (sec)	COMMENTS
Example 15	TEGD,6/6	50/50	19.8	4.8	50	13	77	Solution was clear.
Example 16	TEGD,6/6	50/50	15.4	5.2	50	12	68	Solution was clear.
Example 17	TEGD,6/6	50/50	25.6	5.2	50	14	71	Solution was clear.
Example 18	TEGD,6/6	50/50	15.2	4.8	50	15	93	Solution was clear.
Example 19	TEGD,6/6	76.5/23.5	16.0	5.3	50	15	65	Solution was clear.
Example 20	TEGD,6		12.9	5.2	50	11	44	Solution was clear.
Example 21	TEGD,6		14.0	5.3	50	18	55	Solution was clear.
Example 22	TEGD,6		20.5	5.1	50	20	63	Solution was clear.
Example 23	TEGD,6/6	50/50	19.8	4.9	23	41	121	Solution was clear.
Example 24	TEGD,6/6	50/50	15.4	5.8	23	34	109	Solution was clear.
Example 25	TEGD,6/6	50/50	25.6	5.2	23	32	196	Water became cloudy.
Example 26	TEGD,6/6	50/50	15.2	5.8	23	32	145	Solution was clear.
Example 27	TEGD,6/6	76.5/23.5	16.0	4.7	23	27	152	Solution was clear.
Example 28	TEGD,6		12.9	5.9	23	40	178	Solution was clear.
Example 29	TEGD,6		14.0	4.5	23	30	143	Solution was clear.
Example 30	TEGD,6		20.5	5.9	23	45	178	Solution was clear.

The results above demonstrate the excellent water solubility of the films. The solubility at 50 C is significantly better than at 23 C. The results of Example 25 on the 50/50 copolymer with the highest RV demonstrate that solubility is adversely affected by increasing molecular weight. This is a confirmation of the results of Example 6.

#### Examples 31 to 48

The various polymers in Examples 31 to 48 were prepared using the same procedures already illustrated in Examples 1 to 14 and Comparative Examples A to L but with minor variations in temperature, vacuum and hold time as explained earlier. Films of these polymers were then prepared and their solubility in water were determined as in Examples 15 to 30. The results are tabulated below:

AD 6875 PCT

COMPOSITION	MOLE RATIO	RV	FILM THICKNESS (mls)	WATER TEMP (C)	TIME TO DISINTEGRATE (sec)	TIME TO DISSOLVE (sec)	COMMENTS
Example 31	BGAE,6/TEGD,6/6	32.0	3.3	23	21	101	Solution slightly cloudy.
Example 32	BGAE,6/POE-DPA220,6/6	20.8	2.6	23	12	59	Solution slightly cloudy.
Example 33	BGAE,6/TEGD,6/6	20.4	5.2	23	41	236	Solution slightly cloudy.
Example 34	BGAE,6/TEGD,6/6	18.7	4.7	23	38	145	Solution was clear.
Example 35	BGAE,6/POE-DPA220,6	12.7	6.4	23	50	241	Solution was clear.
Example 36	BGAE,6/POE-DPA220,6/TEGD,6	13.6	5.5	23	29	357	Solution was clear.
Example 37	BGAE,6/POE-DPA220,6/6	13.5	6.0	23	38	401	Solution was clear.
Example 38	POE-DPA220,6/TEGD,6	12.8	4.4	23	27	82	Solution was clear.
Example 39	POE-DPA220,6/BGAE,6	14.9	5.1	23	31	111	Solution was clear.
Example 40	BGAE,6/TEGD,6/6	32.0	3.8	50	8	139	Solution slightly cloudy.
Example 41	BGAE,6/POE-DPA220,6/6	20.8	5.7	50	10	95	Solution slightly cloudy.
Example 42	BGAE,6/TEGD,6/6	20.4	4.5	50	27	69	Solution slightly cloudy.
Example 43	BGAE,6/TEGD,6/6	18.7	5.8	50	22	54	Solution slightly cloudy.
Example 44	BGAE,6/POE-DPA220,6	12.7	5.6	50	16	59	Solution slightly cloudy.
Example 45	BGAE,6/POE-DPA220,6/TEGD,6	13.6	6.7	50	17	109	Solution slightly cloudy.
Example 46	BGAE,6/POE-DPA220,6/6	13.5	6.8	50	14	140	Solution slightly cloudy.
Example 47	POE-DPA220,6/TEGD,6	12.8	5.4	50	5	32	Solution slightly cloudy.
Example 48	POE-DPA220,6/BGAE,6	14.9	5.6	50	13	38	Solution slightly cloudy.

Examples M to T

- Films were prepared and the solubility was determined as in Examples 15 to 30. The results are shown below: "Mostly dissolved" means a breakdown of material as observed, but part of the material did not dissolve.

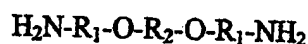
SAMPLE	COMPOSITION	MOL RATIO	RV	FILM THICKNESS (mils)	WATER TEMP (C)	TIME TO DISINTEGRATE (sec)	TIME TO DISSOLVE (hr)
Comparative Example M	TEGD,6/6,6	80/20	15.5	7	23	71	> 5
Comparative Example N	TEGD,12		15.7	6.2	23	No change in 3 hr.	No change in 3 hr.
Comparative Example O	BGAE,6/6	70/30	14.4	5.2	23	94	> 5
Comparative Example P	BGAE,6		13.8	6.1	23	1190	> 5
Comparative Example Q	TEGD,6/6,6	80/20	15.5	5.5	50	16	Mostly dissolved in 5.2 hr.
Comparative Example R	TEGD,12		15.7	5.9	50	No change in 3 hr.	No change in 3 hr.
Comparative Example S	BGAE,6/6	70/30	14.4	6.2	50	24	Mostly dissolved in 4 hrs. Completely dissolved at room temperature
Comparative Example T	BGAE,6		13.8	5.8	50	No change in 3 hr.	No change in 3 hr.

The results above show that solubility alone is not sufficient criterion for packaging applications. The rate of dissolution is much more important for the intended packaging applications.

- 5        It will be readily apparent that any number of variations and modifications to the subject matter disclosed herein can be made, and are contemplated as within the scope and purview of the invention herein.

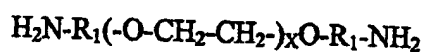
**IN THE CLAIMS**

1. A packaging material comprising a water-soluble polyamide with a solubility in  
5 water at 23 C of at least 1.0 weight percent and derived from the reaction of adipic  
acid and ether diamines with a molecular weight of 148 to 396 and represented by the  
general formulas



10

wherein  $\text{R}_1$  and  $\text{R}_2$  are either  $-\text{CH}_2\text{-CH}_2-$  or  $-\text{CH}_2\text{-CH}_2\text{-CH}_2-$ ;



wherein  $\text{R}_1$  is either  $-\text{CH}_2\text{-CH}_2-$  or  $-\text{CH}_2\text{-CH}_2\text{-CH}_2-$

15

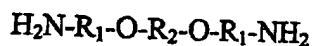
and X has an average value of 2 to 6; and mixtures thereof.

2. The packaging material of Claim 1 further comprising copolyamides of said water-  
soluble polyamide and one or more polyamide forming comonomers.
- 20 3. The packaging material of Claim 1 wherein the water-soluble polyamide is a  
copolymer with caprolactam.
4. The packaging material of Claim 1 in the form of a film, pouch, bag, bottle, or jar.
- 25 5. The packaging material of Claim 1 as a binder material suitable for water-soluble  
tablets and briquettes.
6. The packaging material of Claim 1 wherein said water soluble polyamide has a  
30 relative viscosity of less than 50.

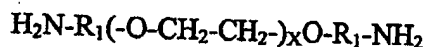


7. The packaging material of Claim 6 wherein the relative viscosity of said water soluble polyamide is between 10 and 35.
8. The packaging material of Claim 1 wherein the solubility in water of said polyamide is at a rate such that a 5-10 mil film formed therefrom will dissolve in less than one hour.
9. The packaging material of Claim 8 wherein the solubility rate is such that a 5-10 mil film will dissolve in less than 30 minutes.
10. A process for the manufacture of water-soluble polyamide packaging materials comprising:

- (i) Forming a water-soluble polyamide as a film, said polyamide having an RV of less than 50, preferably between 10 and 35, solubility in water at 23 C of at least 1.0 weight percent and at such a rate that a 5-10 mil film will dissolve in less than an hour, preferably in less than 30 minutes, and derived from the reaction of adipic acid and ether diamines with a molecular weight of 148 to 396 and represented by the general formulas



wherein  $\text{R}_1$  and  $\text{R}_2$  are either  $-\text{CH}_2-\text{CH}_2-$  or  $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$ ;



wherein  $\text{R}_1$  is either  $-\text{CH}_2-\text{CH}_2-$  or  $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$  and  $x$  has an average value of 2 to 6; and mixtures thereof;

- (ii) Shaping said film so formed in step (i) into a container suitable for placement therein of a material of interest;

(iii) Depositing within said container formed in step (ii) the material of interest; and

5 (iv) Sealing said container so that the material of interest is retained therewithin.

(v)

11. The process of Claim 10 wherein said water soluble polyamide is formed such that it has a relative viscosity of less than 50.

10 12. The process of Claim 11 wherein the relative viscosity of said water soluble polyamide is between 10 and 35.

13. The process of Claim 10 wherein said water soluble polyamide has a solubility such that a 5-10 mil film formed therefrom will dissolve in less than one hour.

15

14. The process of Claim 13 wherein the solubility of said water soluble polyamide is such that the 5-10 mil film will dissolve in less than 30 minutes.

15. The process of Claim 10 wherein the material retained in the container is laundry or dishwasher detergent.

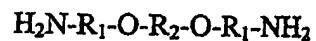
20

16. A process for the manufacture of packaging for materials of interest by including water-soluble polyamide interspersed therewithin comprising:

25 (i) Presenting the material to be packaged;

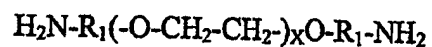
(ii) Interspersing with the material presented in step (i) a water-soluble polyamide having a solubility in water at 23 C of at least 1.0 weight percent and derived from the reaction of adipic acid and ether diamines with a molecular weight of 148 to 396 and represented by the general formulas

30



wherein  $\text{R}_1$  and  $\text{R}_2$  are either  $-\text{CH}_2-\text{CH}_2-$  or  $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$  ;

5



wherein  $\text{R}_1$  is either  $-\text{CH}_2-\text{CH}_2-$  or  $-\text{CH}_2-\text{CH}_2-\text{CH}_2-$

and X has an average value of 2 to 6; and mixtures thereof; and

10

- (iii) Shaping the material in step (i) as interspersed with water-soluble polyamide in step (ii) into a solid form suitable for the application of interest.

17. The process of Claim 16 wherein the solid form is either a tablet or a briquette.

PCT/US 03/15106

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C08J5/18 C08G69/40 C11D17/04

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C08J C08G C11D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 5 866 675 A (AHMED SHARF U ET AL) 2 February 1999 (1999-02-02) column 1, line 11-39 column 2, line 26 -column 5, line 39 column 6, line 6-57; claims; examples	1,2,4-16
X	US 3 882 090 A (FAGERBURG DAVID R ET AL) 6 May 1975 (1975-05-06) column 1, line 6-17 column 1, line 61 -column 4, line 10 column 4, line 42 -column 5, line 33 column 6, line 1-23; claims; examples	1,2,4-16
X	EP 0 773 315 A (FULLER H B LICENSING FINANC) 14 May 1997 (1997-05-14) page 2, line 5-20 page 2, line 39 -page 3, line 51; claims; examples	1,4-15
	-/-	

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

## \* Special categories of cited documents:

\*A\* document defining the general state of the art which is not considered to be of particular relevance

\*E\* earlier document but published on or after the international filing date

\*L\* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

\*O\* document referring to an oral disclosure, use, exhibition or other means

\*P\* document published prior to the international filing date but later than the priority date claimed

\*T\* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

\*X\* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

\*Y\* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

\*A\* document member of the same patent family

Date of the actual completion of the international search

5 August 2003

Date of mailing of the international search report

13/08/2003

Name and mailing address of the ISA

European Patent Office, P.B. 5818 Patentlaan 2  
NL - 2280 HV Rijswijk  
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,  
Fax (+31-70) 340-3016

Authorized officer

Otegui Rebollo, J

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 6 103 809 A (AHMED SHARF U ET AL) 15 August 2000 (2000-08-15) column 1, line 17-33 column 2, line 23 -column 5, line 24 column 8, line 44-54 column 9, line 14 -column 10, line 21; claims; examples	1,2,4-9, 16
X	US 5 863 979 A (AHMED SHARF U) 26 January 1999 (1999-01-26) column 1, line 60 -column 5, line 43; claims	1,2,4-9
X	US 4 735 746 A (SPERANZA GEORGE P ET AL) 5 April 1988 (1988-04-05) column 1, line 13-21 column 2, line 23 -column 4, line 3 column 8, line 12-18; claims; examples	1,2,5-9, 16,17
X	US 5 324 812 A (SPERANZA GEORGE P ET AL) 28 June 1994 (1994-06-28) column 1, line 15-26 column 1, line 63 -column 3, line 9 column 4, line 7 -column 7, line 5; claims; examples 1,2,21-43	1-15
A	EP 0 457 600 A (GRACE W R & CO) 21 November 1991 (1991-11-21) column 1, line 1-47 column 2, line 33-51; claims 6,18	1-15

Patent document cited in search report		Publication date	Patent family member(s)	Publication date
US 5866675	A	02-02-1999	US 5663286 A	02-09-1997
			US 5869596 A	09-02-1999
			US 6103809 A	15-08-2000
			BR 9605432 A	25-08-1998
			CA 2189597 A1	10-05-1997
			DE 69608206 D1	15-06-2000
			DE 69608206 T2	23-11-2000
			EP 0773315 A1	14-05-1997
			JP 3252371 B2	04-02-2002
			JP 9228220 A	02-09-1997
			US 6087550 A	11-07-2000
US 3882090	A	06-05-1975	DE 2426978 A1	19-12-1974
			GB 1463106 A	02-02-1977
			JP 50157496 A	19-12-1975
EP 0773315	A	14-05-1997	US 5663286 A	02-09-1997
			BR 9605432 A	25-08-1998
			CA 2189597 A1	10-05-1997
			DE 69608206 D1	15-06-2000
			DE 69608206 T2	23-11-2000
			EP 0773315 A1	14-05-1997
			JP 3252371 B2	04-02-2002
			JP 9228220 A	02-09-1997
			US 5869596 A	09-02-1999
			US 6103809 A	15-08-2000
			US 6087550 A	11-07-2000
			US 5866675 A	02-02-1999
US 6103809	A	15-08-2000	US 5869596 A	09-02-1999
			US 5866675 A	02-02-1999
			US 5663286 A	02-09-1997
			AU 1593599 A	26-07-1999
			CA 2314482 A1	15-07-1999
			EP 1240252 A2	18-09-2002
			WO 9935189 A2	15-07-1999
			AU 1530899 A	26-07-1999
			EP 1045889 A1	25-10-2000
			WO 9935203 A1	15-07-1999
			BR 9605432 A	25-08-1998
			CA 2189597 A1	10-05-1997
			DE 69608206 D1	15-06-2000
			DE 69608206 T2	23-11-2000
			EP 0773315 A1	14-05-1997
			JP 3252371 B2	04-02-2002
			JP 9228220 A	02-09-1997
			US 6087550 A	11-07-2000
US 5863979	A	26-01-1999	AU 5001897 A	11-05-1998
			WO 9816570 A1	23-04-1998
			AU 7326394 A	22-05-1995
			WO 9512027 A1	04-05-1995
US 4735746	A	05-04-1988	NONE	
US 5324812	A	28-06-1994	NONE	
EP 0457600	A	21-11-1991	AT 143309 T	15-10-1996

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
EP 0457600 A		AU 649039 B2	12-05-1994
		AU 7706291 A	21-11-1991
		CA 2042700 A1	18-11-1991
		DE 69122302 D1	31-10-1996
		DE 69122302 T2	30-04-1997
		EP 0457600 A2	21-11-1991
		JP 3034980 B2	17-04-2000
		JP 4232046 A	20-08-1992
		NZ 238180 A	26-07-1994
		US 6406797 B1	18-06-2002
		ZA 9003650 A	26-02-1992